

The University of Chicago

I. THE ACID STRENGTHS OF ALIPHATIC NITRO COMPOUNDS

II. THE ACIDITY OF AROMATIC NITRO COMPOUNDS IN LIQUID AMMONIA

A DISSERTATION SUBMITTED TO THE FACULTY OF
THE DIVISION OF THE PHYSICAL SCIENCES IN
CANDIDACY FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

DEPARTMENT OF CHEMISTRY
JUNE, 1945

By
JOHN DAVIES FARR

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ACKNOWLEDGMENT

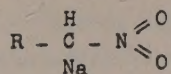
The author wishes here to thank Dr. G. W. Wheland under whose direction this work was conducted.



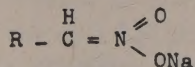
I. THE ACID STRENGTHS OF ALIPHATIC NITRO COMPOUNDS

The acidic nature of the primary and secondary nitroparaffins has been known for a long time. The first direct measurement of the ionization constants of some of these compounds was made by Junell (1). He found that the acidity appeared to increase in the order: nitromethane < nitroethane < 2-nitropropane. Owing to the decomposition of 2-nitropropane in alkaline solution, he could not obtain reproducible results for this compound. However if this order of increasing acidity with the addition of a methyl group is correct, the nitroparaffins behave in a manner just the reverse of the carboxylic acids. It was therefore decided that the ionization constants at 25°C. of nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane should be measured in an effort to obtain more information about this anomalous behavior. During the course of the work, Maron and Turnbull published values of the ionization constants of nitromethane, nitroethane, and 2-nitropropane (2). The values of these workers are in satisfactory agreement with those found in this laboratory although the discrepancy for nitroethane is somewhat larger than the probable error in either set of measurements.

The fact that the primary and secondary aliphatic nitro compounds dissolve in alkali was discovered by Victor Meyer (3). He attributed this to the effect of the nitro group on the carbon atom which caused the hydrogen on that atom to be acidic. For the sodium salt he gave the structure

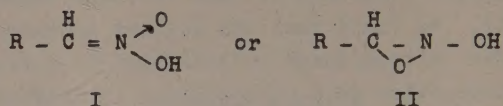


Michael on the basis of analogy to the known keto-enol equilibrium thought the salt to be (4)



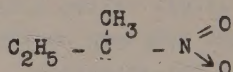
It was reported by Nef that the sodium salt behaved as if it were

formed from a much stronger acid than the nitro compound appeared to be (5). As will be discussed below, this view of Nef's is now known to be incorrect. Further light was shed on the problem of the nitroparaffins by Hantzsch who isolated phenylnitromethane in two forms, thus showing that the nitro compounds can exist in two tautomeric forms in an equilibrium that parallels the keto-enol equilibria (6). However some controversy still remained as to whether the more acid form has the structure

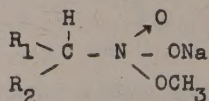


The latter structure (II) is not generally accepted now as it does not seem probable that a substance with such a structure could exist in a readily reversible equilibrium with the nitro form. Also formula I better shows the similarity between the nitro compounds and the keto-enol systems.

Some interesting work on salt formation was done by Kuhn and Albrecht (7). They treated the optically active compound 2-nitrobutane with sodium methoxide in methyl alcohol. Now, if salt formation occurs and if structure I above loses a proton to form this salt, the solution should lose its activity. These workers found that a salt is formed which is still optically active. However if aqueous sodium hydroxide is used the activity disappears. Kuhn and Albrecht believed the anion to have the structure



where the two unshared electrons on the -carbon atom act as a fourth group. This is not a very satisfactory explanation and another possibility has been proposed (8). The product of the reaction between sodium methoxide and a nitro compound may not be the sodium salt expected but rather the following compound



Since this mechanism affects only the nitro group, it would be interesting to see what effect sodium methoxide has on the optical rotatory power of an active, tertiary nitro compound.

Experimental

Materials

The nitromethane and nitroethane were Eastman Kodak practical grade. The 1- and 2-nitropropane were kindly furnished by the Commercial Solvents Corporation. These compounds were fractionated in a 60 centimeter column packed with glass helices. The following fractions were used:

TABLE 1

Compound	Temperature	Pressure
CH_3NO_2	100°C.	744 m.m.
$\text{C}_2\text{H}_5\text{NO}_2$	114-114.5	750
1- $\text{C}_3\text{H}_7\text{NO}_2$	131-131.5	747
2- $\text{C}_3\text{H}_7\text{NO}_2$	119.7-120	742

The inorganic materials were of analytical reagent grade purity. All solutions were made with boiled distilled water.

Method

The ionization constants of the nitro compounds were obtained in the following way. To a solution of the nitro compound in water, standard base was added. The pH of this solution was determined with a glass electrode after time had been allowed for equilibrium to be reached. In this manner a complete titration curve was obtained and the ionization constant determined from it. Usually, however, several points were determined in the vicinity of half-neutralization and the pH determined at half neutralization from the graph of E.M.F. versus the amount of base added. This value of the pH is equal to the pK after correction for hydrolysis and salt effects. The buffer action of the solution is greatest at half neutralization and this would tend to minimize any errors either in the determination of concentration

or due to the presence of impurities.

The solutions of the nitro compound were prepared by weighing a sample of the nitroparaffin in a 100 cc. volumetric flask, and then diluting to volume with water. The concentrations employed ranged from 0.1 to 0.01 molar.

Apparatus

The glass electrode was the bulb type with an inner electrode of Ag - AgCl in 0.1 N hydrochloric acid. The reference electrode was a saturated calomel electrode, Leeds and Northrup assembly number 7724. Both the calomel and glass electrodes were inserted in a rubber stopper which fitted into a 200 cc. lipless beaker. A stirrer and the tip of a burette were also passed through this stopper. The beaker with a measured amount of a nitroparaffin solution in it, and with the electrodes placed in it, was put in an oil thermostat kept at $25.0^{\circ} \pm 0.1^{\circ} \text{C.}$ during measurements. The E.M.F. of the cell assembly used is given by

$$E = E_0 + \frac{2.303 RT}{nF} (\text{pH})$$

In order to determine the cell constant, E_0 , a Sorenson buffer of pH 8.25 was used (9). Another Sorenson buffer of pH 9.96 was also used to check the extrapolation into the pH range in which the measurements were made. Owing to the appreciable sodium ion error in solutions of pH above nine, barium hydroxide was used as the standard base.

The E.M.F. of the cell was measured on a Leeds and Northrup portable potentiometer-electrometer number 7760. This instrument could be read to 0.01 pH unit. The entire apparatus was enclosed in a grounded metal cabinet.

Additional Procedures

To some of the solutions an excess of base was added. Then after the E.M.F. became constant, sufficient standard hydrochloric acid was added to bring the solution to half-neutralization. The E.M.F. was measured here to see if the same equilibrium was reached from both sides. It was found that the values agreed.

The usual procedure of titrating at 25°C. could not be used with the solutions of 2-nitropropane since it decomposes

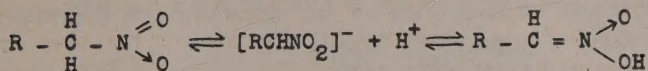
somewhat in alkaline solution. The procedure for this compound was to half-neutralize its solutions at 0°C . and allow them to stand 18-24 hours in a refrigerator. The pH measurements were made at 25° . The completely neutralized solutions were prepared in the same manner and then half-neutralized at 0°C . with acetic acid solution. After these solutions had been allowed to stand another 18-24 hours in the refrigerator, their pH was measured at 25° .

In order to determine the decomposition products of 2-nitropropane in alkali, a 0.1 molar solution of this compound was refluxed with excess base for five hours. The solution was cooled, just acidified, and then distilled. A blue liquid which changed to a white solid in the condenser distilled out initially. This was the pseudonitrole ($\text{CH}_3-\overset{\text{NO}}{\underset{\text{NO}_2}{\text{C}}}-\text{CH}_3$) as shown by its melting point and nitrogen analysis. The appearance of this compound indicated that both 2-nitropropane and nitrous acid had been present. The distillate was treated with 2, 4 dinitrophenylhydrazine (10). In this way it was found that 81 per cent of the 2-nitropropane had been converted to acetone and 4 per cent was recovered in the form of the pseudonitrole. The residue from the distillation was extracted with ether and from this a sticky brown solid of unknown composition was obtained.

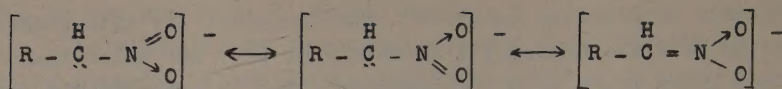
Some half-neutralized solutions of 2-nitropropane were allowed to stand at room temperature for 48 hours. They were then tested for acetone by means of Nessler's reagent (11). An amount of acetone corresponding to 2 per cent decomposition of the nitro compound was observed. Some other solutions were prepared at 0° and left in the refrigerator for 24 hours. Only a trace of acetone could be detected in these.

Equations and Calculations

Since nitroparaffins can exist in two tautomeria forms the following equilibria occur in a solution:



The anion, $[\text{RCHNO}_2]^-$, is a resonance hybrid of the three following structures:



The ionization constant measured in aqueous solution then is an apparent ionization constant defined by

$$K_A = \frac{[\text{H}^+] [\text{RCHNO}_2^-]}{[\text{RCH}_2\text{NO}_2] + [\text{RCHNO}_2\text{H}]}$$

According to Maron (12), the amount of aci form at equilibrium is negligible so that K_A reduces to the usual equilibrium constant, K .

$$K = \frac{[\text{H}^+] [\text{RCHNO}_2^-]}{[\text{RCH}_2\text{NO}_2]}$$

The equations used for the calculations involved in this work are given below together with a sample calculation.

$$K = \frac{[\text{H}^+] (X^-) \gamma_{\pm}}{(\text{HX})}$$

$$\text{pK} = \text{pH} - \log \frac{(X^-)}{(\text{HX})} - \log \gamma_{\pm}$$

$$(X^-) = a \cdot c + (\text{H}^+) - (\text{OH}^-)$$

$$(\text{HX}) = (1-a)c - (\text{H}^+) + (\text{OH}^-)$$

$$- \log \gamma_{\pm} = 0.506 \mu^{1/2}$$

$$\mu = 1/2 \sum C_i Z_i^2$$

[] denotes activity.

() denotes concentration.

pK is the thermodynamic dissociation constant.

pH is the negative logarithm of the hydrogen ion activity.

a is the ratio $\frac{\text{equivalents base}}{\text{equivalents acid}}$

C is the total concentration of the nitro compound.

$\gamma_{\pm}$ is the mean activity coefficient.

C_i is the molar concentration of the i th ion.

Z_i is the valence of the i th ion.

μ is the ionic strength.

Sample Calculation

TABLE 2

1	2	3	4	5
0.6276g.	0.01028N	0.4962	0.2140	0.4815V.
.....			0.2422	0.4861
.....			0.2719	0.4915

1. Weight of sample of nitromethane.
2. Concentration of solution of nitromethane.
3. Number of milliequivalents of nitromethane used in measurement.
4. Number of milliequivalents of standard base added to 3.
5. E.M.F. observed for the solution.

From the graph of E.M.F. versus the number of milliequivalents of base added (Fig. 1), the E.M.F. at one half neutralization is 0.4872 volts. The calculations involved in the conversion of this E.M.F. to a pH value and the correction of this pH for hydrolysis and salt effects follow.

$$\text{pH} = \frac{E + E_0}{0.05915}$$

$$= \frac{0.4872 + 0.1161}{0.05915}$$

$$\text{pH} = 10.19$$

$$(X^-) = (a \cdot c) + (H^+) - (OH^-)$$

$$= 0.00409 + 6.3 \times 10^{-11} - 0.00016$$

$$(X^-) = 0.00393 \text{ moles/liter}$$

$$(HX) = (1-a)c + (OH^-) - (H^+)$$

$$= 0.00409 + 0.00016 - 6.3 \times 10^{-11}$$

$$(HX) = 0.00415 \text{ moles/liter}$$

$$\log \frac{X^-}{HX} = 9.9764 - 10$$

$$- \log \frac{X^-}{HX} = 0.0239$$

$$= 1/2 \sum c_1 z_1^2$$

$$= 1/2 \sum \frac{(0.00409)(2)^2}{2} + 0.00393(1)^2 + (1.6 \times 10^{-4})(1)^2$$

$$= 0.00613$$

$$- \log \gamma_{\pm} = 0.506 \mu^{1/2}$$

$$= 0.0396$$

$$pK = pH - \log \frac{X^-}{HX} - \log \gamma_{\pm}$$

$$= 10.19 + 0.0239 + 0.04$$

$$pK = 10.25$$

In the above the ion product constant for water is taken as 1.008×10^{-14} at 25° from the work of Harned and Owen (13). The table below is a summary of the data obtained:

TABLE 3

	1	2	3	4	5
$\text{CH}_3\text{NO}_2 \dots$	10.22	10.22	10.22	± 0.03	8
$\text{C}_2\text{H}_5\text{NO}_2 \dots$	8.59	8.61	8.60	± 0.02	8
$1\text{-C}_3\text{H}_7\text{NO}_2 \dots$	8.99	8.97	8.98	± 0.02	4
$2\text{-C}_3\text{H}_7\text{NO}_2 \dots$	7.89	7.87	7.88	± 0.05	5

1. Corrected pK obtained from half-neutralization.
2. Corrected pK obtained from complete neutralization followed by addition of acid.
3. Average of 1 and 2.
4. Mean deviation.
5. Number of measurements made for each figure in 1 and 2.

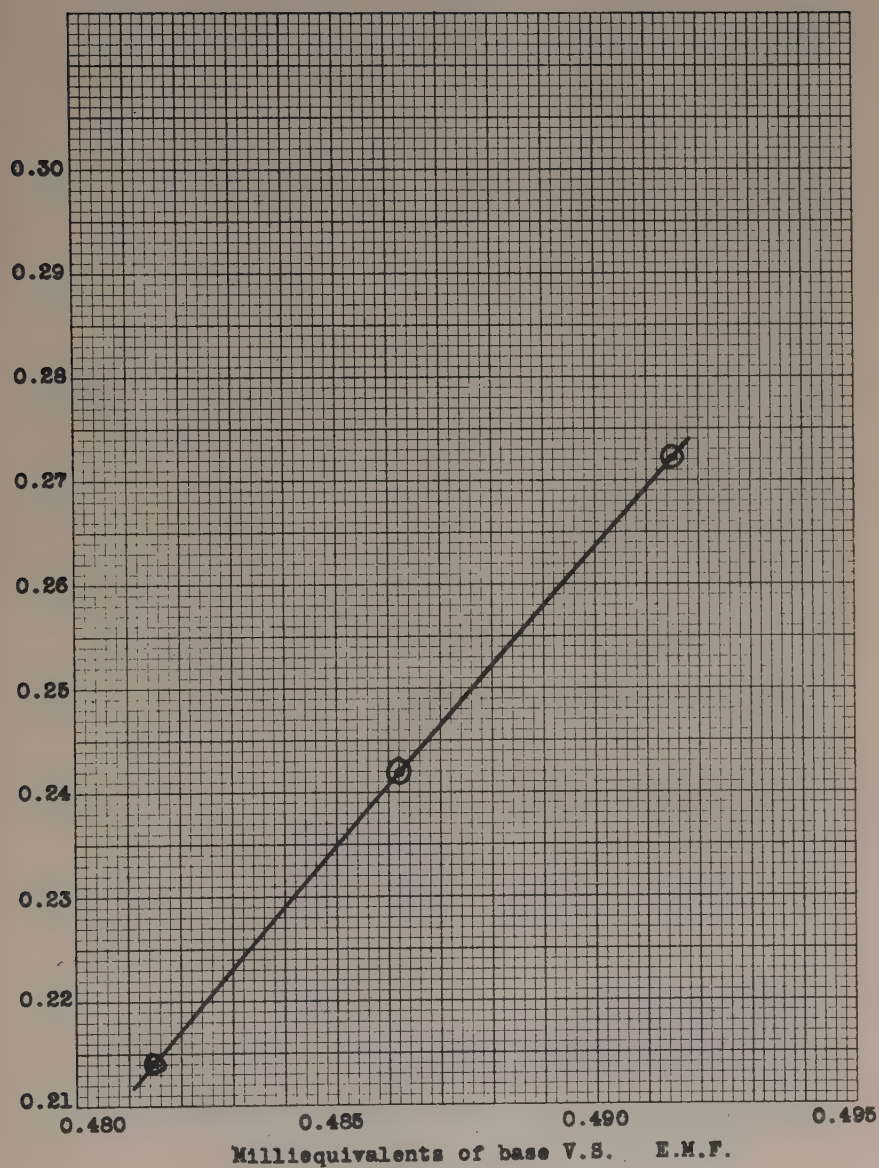


Figure I

where e is the charge on the anion,

ϵ is the dielectric constant,

N is anogadro's number,

r is the radius of the anion, and

ΔE_N is the non-electrostatic energy change (16).

Since this equation did not fit the experimental data too well, Kirkwood and Westheimer developed an expression for the same process (17). They considered the problem by way of the dipole field at the ionizable proton. Westheimer et al. have applied this approach to a large number of acids with success (18). In the light of this work, the variation of the acidity of the nitroparaffins can be explained qualitatively.

The acidity of the aliphatic nitro compounds is probably due mainly to the electrostatic interaction between the nitro group and the acidic hydrogen. Resonance may also play a part in the acidity as it does in the analogous keto-enol equilibria, but the main cause appears to be an electrostatic effect. The effect of the nitro group is transmitted both through the molecule and through the solvent. In the case of nitromethane the lines of force between the nitro group and a proton must pass mainly through the solvent, a region of high dielectric constant. In 2-nitropropane on the other hand some of these lines of force will pass through the two adjacent methyl groups, a region of low dielectric constant. This will increase the electrostatic interaction in 2-nitropropane over that of nitromethane and likewise increase the acidity. One would expect then that nitroethane and 1-nitropropane would be between nitromethane and 2-nitropropane in acidity. This has been found to be in agreement with the experimental results. The terminal methyl group exhibits its usual inductive effect in 1-nitropropane by making it a weaker acid than nitroethane.

The ionization constants of the aci forms of the nitroparaffins have been shown to behave in a manner entirely analogous to those of the carboxylic acids (19). In the aci form the lines of force between the nitro group and the acidic proton can be expected to pass mainly through the solvent so that the usual inductive effects of methyl groups will determine the variation in acidity in the series.

Summary

1. The pK_s of nitromethane, nitroethane, 1 nitropropane, and 2-nitropropane were measured in aqueous solution at $25^{\circ}C$.

2. An explanation of the anomalous acidities of these compounds is offered.

The Ionization Constant of Phenol

Phenol of analytical reagent grade was distilled in an all glass apparatus under exclusion of moisture. The material boiling at 176° uncorrected was used for the work. This sample was stored in a vacuum desiccator containing phosphoric anhydride. The phenol for a measurement was transferred rapidly to a weighed volumetric flask. The procedure for a measurement of the ionization constant was the same as that used with the nitro compounds in this thesis. The results obtained at $25.0^{\circ}C$. are summarized in the following table:

TABLE 4

1	2	3	4
9.98	9.93	9.96	$\pm .02$

1. The average of five measurements, corrected for hydrolysis and salt effects, obtained from half-neutralized solutions.
2. The average of four measurements made on solutions which were prepared by first adding an equivalent amount of base to neutralize the phenol and then adding sufficient acid to bring the solution back to half-neutralization.
3. The average of 1 and 2.
4. The mean deviation.

Literature values for phenol

9.89 (25°) Walker and Cormack, J.C.S., 77, 5 (1900).

9.97 (25°) Kendall, J.A.C.S., 39, 7 (1917).

9.94 (18°) Mizutani, Z. Phys. Chem., 118, 318 (1925).

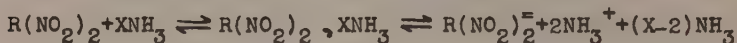
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Westheimer, J. Am. Chem. Soc., 61, 1977 (1939).
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II. THE ACIDITY OF AROMATIC NITRO COMPOUNDS IN LIQUID AMMONIA

Introduction

When m-dinitrobenzene is dissolved in liquid ammonia, it forms initially a dark blue solution which slowly changes in color to become a dark red. This solution has a surprisingly high conductivity. The limiting molar conductance for a salt such as potassium nitrate in ammonia is around $340 \text{ ohm}^{-1} \text{ cm}^2$ per mole while the corresponding value for m-dinitrobenzene is approximately $240 \text{ ohm}^{-1} \text{ cm}^2$ per mole (1). In order to investigate this phenomenon, Field, Garner, and Smith electrolysed the ammonia solution and found that the organic material migrates toward the anode; that there is no evolution of gas at either electrode; and that the organic material can be recovered unchanged (2). To explain these observations they postulated the following reaction:



According to their interpretation, $\text{R}(\text{NO}_2)_2^{\cdot-}$ gives up its extra electrons at the anode and becomes $\text{R}(\text{NO}_2)_2$. The NH_3^+ gains an electron at the cathode to form ammonia. If these workers are correct, free radicals exist in the solution and it should be possible to detect them by measuring the magnetic susceptibility of m-dinitrobenzene in liquid ammonia. This work was attempted but no satisfactory results were obtained from it owing to the slight solubility of this compound in ammonia. The experimentally measured effect was not much larger than the apparent experimental error. M-dinitrobenzene also behaves as an electrolyte in hydrazine and ethylene diamine solutions. Consequently magnetic measurements were attempted on these solutions, but owing to the decomposition of m-dinitrobenzene in these solvents, the work was abandoned.

The electrolysis of m-dinitrobenzene in liquid ammonia was then repeated. Contrary to the results of Field, Garner, and

Smith it was found that there is gas evolved at both electrodes and that the m-dinitrobenzene can not be recovered unchanged after the electrolysis. In agreement with the other workers, it was observed that the intensity of the color of the solution around the cathode decreased during the course of electrolysis. This indicates that the organic compound forms the anion in the solution.

Experimental

Materials

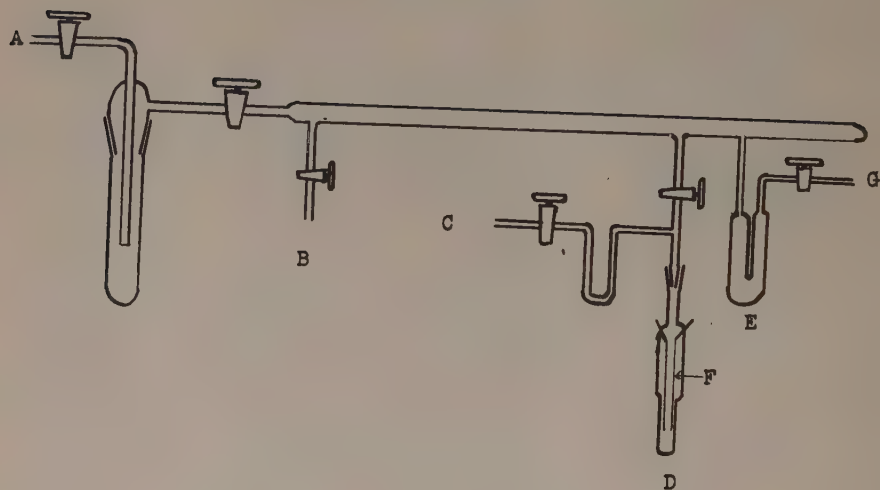
The meta-dinitrobenzene, a commercial preparation, was recrystallized from alkaline alcohol to remove any thiophene derivatives. It was then recrystallized from distilled water and sublimed in vacuum. Commercial ammonia, stored in a steel cylinder over sodium, was used as the solvent.

Apparatus

The solutions were prepared in a vacuum line which consisted essentially of an inlet for the ammonia, a U-tube containing sodium, the electrolysis cell, and a Töpler pump besides the mercury diffusion pump and a fore pump (Fig. II). The electrolysis cell had two platinum electrodes spotwelded to two tungsten wires which were sealed through the glass wall of the cell. A silver coulometer was used to measure the amount of current passing through the solution. A potential of 18 volts was used for the electrolysis. For the analysis of the gas evolved during the experiment, a water-jacketed gas burette with two platinum electrodes was employed. Water was used as the confining liquid. Alkaline pyrogallol solution in a Hempel double absorption pipette was used for the oxygen determinations. Hydrogen was determined by explosion with hydrogen-free oxygen. The residue was assumed to be nitrogen.

Procedure

For a measurement, approximately 0.1 gram of m-dinitrobenzene was placed in the electrolysis cell which was then connected to the vacuum line by means of a 12/30 standard taper. The apparatus was then evacuated to 10^{-5} mm. for several hours. Baths of liquid ammonia in unsilvered dewars were used to condense



- A. To pumping system
- B. To McLeod gauge
- C. To Töpler pump
- D. Electrolysis cell
- E. U-tube
- F. PT electrode
- G. Ammonia inlet

Figure II

ammonia in the line. By drawing air over the surface of a bath, its temperature could be lowered 20°C . The ammonia to be used as the solvent was expanded into the line from the storage tank which was sealed vacuum-tight with picene to the line. This ammonia was then condensed in the U-tube containing sodium until 6-7 cc. had been collected. A nichrome wire heater was placed in the bath surrounding this U-tube and the ammonia was distilled into the electrolysis cell which was immersed in a cooled ammonia bath. The ammonia solution of m-dinitrobenzene was degassed twice by freezing it with liquid nitrogen and evacuating the cell. The solutions were electrolysed at the boiling point of ammonia. Upon completion of the electrolysis the solutions were again frozen with liquid nitrogen and any gas in the apparatus was transferred by means of the Töpler pump to a burette where the total volume of gas was measured over mercury. Most of the gas was then forced into the gas analysis apparatus and its composition determined. The following table gives the results of the gas analysis. All volumes are corrected to 0°C . 760 mm.

TABLE 5

1 Experi- ment	2 Volume	3 V_{O_2} obs.	4 V_{H_2} obs.	5 V_{N_2}	6 Faradays	7 V_{H_2} Calcd.	8 V_{N_2} Calcd.
I	4.65cc.	0.0cc.	2.90cc.	2.05cc.	0.000586	6.56cc.	2.19cc.
II	9.95	0.0	5.68	3.77	0.001068	11.93	3.98
III A	2.46	0.0	1.11	1.35	0.000460	5.15	1.72
III B	11.27	0.0	6.73	4.54	0.001205	13.50	4.50

In column 1 is the number of the experiment. Experiment III was divided into two parts. That is the electrolysis was interrupted and the gas evolved was removed and then the electrolysis was resumed.

In column 2 is the total volume of gas evolved during the electrolysis.

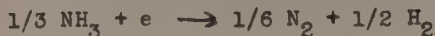
In column 3 is the volume of oxygen found by analysis of 2.

In column 4 is the volume of hydrogen found by analysis of 2.

In column 5 is the volume of nitrogen found by analysis of 2.

In column 6 is the number of Faradays which passed through the solution.

In column 7 is the volume of hydrogen calculated from the number of coulombs used and the following reaction



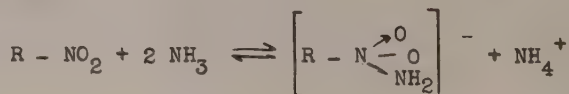
In column 8 is the volume of nitrogen calculated as in column 7.

The observed values for hydrogen are all quite low while those for nitrogen are in fair agreement with the calculated values for them. In experiment III A only 22 per cent of the calculated volume of hydrogen was found while in III B this value rose to 50 per cent. Since experiment III B was allowed to run a much longer time than III A the concentration of the anion around the cathode was kept at a lower value for a longer period of time in III B. As a result more of the hydrogen evolved at the cathode could escape from the solution. The organic residue left after the electrolysis was slightly darkened. This material gave a test for an aromatic amine (3). Apparently some hydrogen is used up in reducing the nitro compound. The residue from experiment I gave a very faint test for nitrite ion (4). In none of the others could this test be duplicated. If nitrites are formed, the low values of the nitrogen analyses would be explained. Goldschmidt electrolysed liquid ammonia solutions of phenol and other organic acids and generally obtained a lower value for the nitrogen than expected (5).

A blank electrolysis was run on the ammonia in which the usual procedure of preparing a solution was followed with the omission, of course, of the m-dinitrobenzene. No current could be detected on a milliammeter when either an 18 volt or 110 volt potential was applied to the ammonia. The solutions of m-dinitrobenzene usually had a current of 20-30 milliamperes flowing through them under a potential of 18 volts.

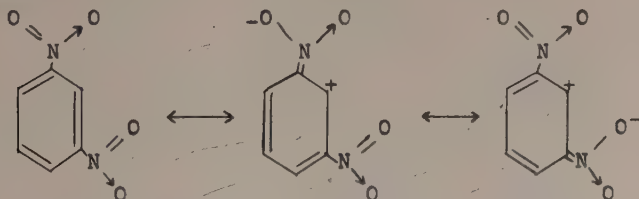
Discussion

On the basis of the work in this thesis, m-dinitrobenzene behaves like an acid with an ionizable proton. A conceivable explanation of this would be that ionization occurs in accordance with the scheme



The above equation would account for the existence of the organic compound in the anion and the presence of ammonium ion. However, this structure does not indicate that it is necessary for two nitro groups to be situated on the same aromatic ring and that these two groups be meta to each other for the compound to exhibit a high conductivity in ammonia. Also a marked color change would not be expected on the present basis. The above reaction may occur with the O- and P-dinitrobenzenes in ammonia since these compounds form slightly yellowish solutions and have a very low molar conductivity. In hydrazine solution this reaction possibly does take place to a greater extent since Walden found a conductivity comparable to a dibasic acid in the same solvent for all three of the dinitrobenzenes (6). The O- and P-compounds form colorless solutions in hydrazine while the M compound forms a dark blue solution.

Another possible explanation for the conductivity of the ammonia solutions is that one of the nuclear hydrogen atoms can dissociate as a proton. In m-dinitrobenzene the resonance effects of the two nitro groups combine to increase the positive potential in the neighborhood of the hydrogen atoms on the ortho and para compounds.

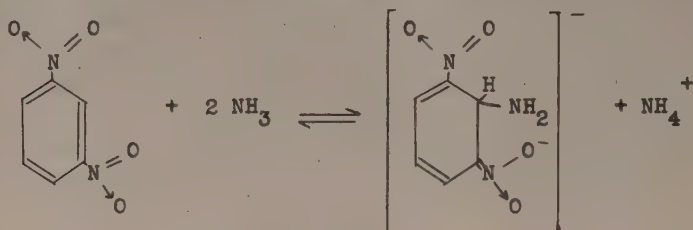


Hantzsch and Kissel converted trinitrotoluene into its potassium salt in methyl alcohol and then by adding acid to this salt at a low temperature, they were able to obtain the free acid (7). The analysis of this compound corresponded to an addition compound between methyl alcohol and trinitrotoluene. They were also able to prepare an acetyl derivative of this acid. This indicates the presence of a hydroxyl group. The above explanation does not fit these facts. Walden has found that trinitrobenzene and trinitro-m-xylene have approximately the same molar conductance in hydrazine and this conductivity of a tribasic acid in hydrazine (8). Therefore there is no correlation between the

conductivity and the number of nuclear hydrogen atoms in hydrazine solutions. However, Hantzsch and Caldwell found that both trinitrobenzene and trinitrotoluene exhibit a very slight conductivity in pyridine where presumably this method of ionizing is the only explanation (9).

By analogy then to the above, it would not be expected that this mechanism of losing a proton would play an important part in ammonia solutions.

There is then left the possibility of the formation of a quinoid compound of the type proposed by Meisenheimer (10). The reaction involved in this interpretation is the following:



This scheme makes the organic compound an anion that would be colored. The formation of hydrogen in the electrolysis is also explained by the presence of ammonium ion. Besides the structure given above there are two others possible in which the amino group is ortho to one nitro group and para to the other nitro group and therefore these two are indistinguishable from one another. All of these possibilities have two resonance structures. The particular form given above may be stabilized by double chelation between the hydrogen atoms on the amino group and the adjacent oxygens of the two nitro groups (11). The ortho and para dinitrobenzenes do not have this possibility for double chelation nor do they have two equivalent resonance structures for each of the various isomers to stabilize the anion. Consequently they behave as very poor electrolytes in liquid ammonia.

The color of a solution of a meta dinitro compound in liquid ammonia is decreased if there is a methyl group ortho to one of the nitro groups and almost inhibited if there are two methyl groups ortho to one of the nitro groups (12). This would be expected on the basis of a quinoid salt formation since methyl groups are known to have a damping effect on this type of resonance structure (13).

Magnetic Measurements

The magnetic susceptibility of m-dinitrobenzene in liquid ammonia at -33°C . was measured by the Gouy Method. The apparatus and procedure were those of Freed and Sugarman (14) with the following minor modifications. The tube in which the solution is prepared was put on the vacuum line by means of a standard taper for convenience in introducing the m-dinitrobenzene. The volume of ammonia used in the preparation of a solution was not measured but instead the Gouy tube was used as a pycnometer to determine the density and also the concentration of the solution. The amount of m-dinitrobenzene in a solution was determined by allowing a weighed amount of the solution to evaporate and then the residue was weighed.

Under the conditions used in this experiment, the force on an object in a magnetic field is given by

$$F = 1/2 K q H^2$$

where F is the force,

K is the volume susceptibility,

q is the cross sectional area of the object,

and H is the field strength (15).

If this force is measured at a series of field strengths with a known substance, a value of $qH^2/2$ can be calculated for each current strength used. If it is assumed that the field strength is a reproducible function of the current, a plot of the force on another material against $qH^2/2$ should be a straight line whose slope is the volume susceptibility of this other material. This procedure was followed in the calculations and the method of least squares was employed to find the slope.

A sample calculation follows.

TABLE 6

1	2	3	4	5
I	ΔW	E.E.	N.E.	$\frac{gH^2}{2}$
3.0 amp.	-0.061 mg.	-0.020 mg.	-0.041 mg.	3,500
6.0	-0.214	-0.156	-0.058	12,050
8.8	-0.338	-0.265	-0.073	19,850
11.95	-0.416	-0.340	-0.076	26,000
15.7	-0.496	-0.416	-0.080	30,500

1. Current through field coils of the magnet.
2. The apparent change in weight of the Gouy tube in milligrams.
3. The end effect correction for the change in weight of the Gouy tube owing to dissymmetry of the tube and the magnetic field.
4. The net effect which is column 2-column 3.
5. The values of $\frac{gH^2}{2}$ obtained from a calibration with ammonia (16).

Since this is a differential method, the susceptibility, K_1 , of the solution minus the susceptibility, K_2 , of the solvent is observed. For the data above this was found to be -1.303×10^{-8} .

$$K_1 - K_2 = -1.303 \times 10^{-8}$$

$$K_1 = -0.6633 \times 10^{-6} - 0.0130 \times 10^{-6}$$

$$K_1 = -0.6763 \times 10^{-6}$$

$$\chi_1 = \frac{K_1}{D_1}$$

$$\chi_1 = \frac{-0.6763 \times 10^{-6}}{.6860}$$

$$= -0.9858 \times 10^{-6}$$

$$\chi_1 = G_2 \chi_2 + G_3 \chi_3$$

$$-0.9858 \times 10^{-6} = (0.992)(-0.9667 \times 10^{-6}) + (0.0078) \chi_3$$

$$\chi_3 = \frac{-0.9266 \times 10^{-6}}{.0078}$$

$$= -3.41 \times 10^{-6}$$

χ_1 is the mass susceptibility of the solution.

χ_2 is the mass susceptibility of the solvent.

χ_3 is the mass susceptibility of the m-dinitrobenzene.

D_1 is the density of the solution.

G_2 is the number of grams of solvent per gram of solution.

G_3 is the number of grams of solute per gram of solution.

A summary of the data obtained follows:

TABLE 7

1	2	3
0.0149	0.6794	-10.0
0.0464	0.6860	- 3.41
0.0608	0.6862	- 0.724
0.0673	0.6869	- 1.15
0.0715	0.6874	- 1.02

1. The concentration of the solution in moles / liter.
2. The density of the solution.
3. The mass susceptibility of m-dinitrobenzene $\times 10^{-6}$. The literature value is -0.398×10^{-6} .

Clearly no conclusions can be drawn from such unreproducible data. During the course of the work, the magnetic susceptibility of ethylene diamine was measured. It was found to have a mass susceptibility of -0.7709×10^{-6} at 25° .

Summary

1. The electrolysis work of Field, Garner, and Smith on solutions of m-dinitrobenzene in liquid ammonia was repeated and results that differed from those of these workers were obtained.

2. An explanation for the conductivity of aromatic nitro compounds in liquid ammonia is offered.

3. An unsuccessful attempt was made to measure the magnetic susceptibility of m-dinitrobenzene in liquid ammonia.

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